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(54) [Title of the Invention]

Polyester Resin Composition and Process for the Production of Sheet

(57) [Abstract]

[Object]

It is to provide a polyester resin composition having a specific non-crystalline polyester resin as a main component with a melt tension enabling its thin and wide sheets having excellent transparency to be peeled off from metal rollers at a high temperature and at the same time, excellent peelability from the rollers by compounding it with a specific resin, which can raise and control the melt viscosity.

[Solution]

A polyester resin composition characterized by containing 100 parts by weight of a non-crystalline polyester resin comprising a dicarboxylic acid component composed of terephthalic acid and diol component composed of 20-35 mole% of 1,4-cyclohexanedimethanol and 65-80 mole% of ethylene glycol as a major component; 1-17 parts by weight of an acrylic rubber type modifying agent and 1-3 parts by weight of a lubricant.

[Patent Claims]

[Claim 1]

A polyester resin composition characterized by containing 100 parts by weight of a non-crystalline polyester resin comprising a dicarboxylic acid component composed of terephthalic acid and diol component composed of 20-35 mole% of 1,4-cyclohexanedimethanol and 65-80 mole% of ethylene glycol as a major component; 1-17 parts by weight of an acrylic rubber type modifying agent and 1-3 parts by weight of a lubricant.

[Claim 2]

A polyester resin composition characterized by containing 100 parts by weight of a non-crystalline polyester resin comprising a dicarboxylic acid component composed of terephthalic acid and diol component composed of 20-35 mole% of 1,4-cyclohexanedimethanol and 65-80 mole% of ethylene glycol as a major component; 0.5-17 parts by weight of an acrylic rubber type modifying agent, 0.5-10 parts by weight of an acrylic processing aid material having methyl methacrylate as a main component and 1-3 parts by weight of a lubricant.

[Claim 3]

The polyester resin composition of Claim 1 or 2, wherein the resin components are 60-100 wt% of the non-crystalline polyester and 0-40 wt% of other polyester.

[Claim 4]

The polyester resin composition of Claim 1 or 2, wherein the resin components are 80-100 wt% of the non-crystalline polyester and 0-20 wt% of other polyester.

[Claim 5]

The polyester resin composition of Claim 1-4, wherein the polyester resin composition is a composition for calendering.

[Claim 6]

A process for the production of sheets characterized by carrying out calendering of the polyester resin composition of Claim 1-5.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of the Invention]

This invention pertains to a polyester resin composition having a satisfactory melt-molding workability at the time of calender or extrusion molding. In particular, it pertains to a poly-

ter resin composition provided with a satisfactory melt tension enabling its thin and wide films to be peeled off from metal rollers and showing excellent peelability from the rollers.

[0002]

[Prior Art]

The applications of polyester resin sheets are being expanded to surface decoration applications of light electrical products such as refrigerators, television cabinets, etc., and surface materials of furniture, doors, shelves, etc., as well as packing materials of food and drug products, etc. Such polyester resin sheets have been conventionally prepared by carrying out extrusion sheet molding of molten resin pellets. In the case of this extrusion molding method, a sheet of a certain constant thickness is extruded through a T-die and treated with casting rollers controlled at a temperature below the glass transition temperature to form a sheet of a desired thickness. The sheet-molding speed is relatively slow, and the productivity is not necessarily good.

[0003]

Polyester resins have a shortcoming of adhering strongly to heated rollers in the case of sheet preparation by carrying out calendering or secondary processing of sheets such as thermal lamination, thermal embossing, etc. To eliminate this shortcoming, Japanese Kokai Patent Application Publication No. Hei 11[1999]-343,353 discloses a method to inhibit adhesiveness at the time of calendering by using a fatty acid ester-type lubricant enabling to carry out calendering. However, the melt viscosity is not too high even after the addition of such a fatty acid ester-type lubricant, and consequently, there is still a shortcoming of being able to carry out calendering of sheets of only about 0.3 mm thick at a relatively low temperature and low production speed. Therefore, a composition increasing melt viscosity, enabling to carry out high-temperature processing and providing a thin sheet of less than 0.1 mm thick was invented by compounding an acrylic silicone rubber modifying agent, but there was a shortcoming of inferior transparency.

[0004]

[Object of the Invention]

The object of this invention is to provide a polyester resin composition having a specific non-crystalline polyester resin as a main component with a melt tension enabling its thin and wide sheets having excellent transparency to be peeled off from metal rollers at a high temperature and at the same time, excellent peelability from the rollers by compounding it with a specific resin, which can raise and control the melt viscosity.

[0005]

[Means to Accomplish the Object]

This invention provides a polyester resin composition characterized by containing 100 parts by weight of a non-crystalline polyester resin comprising a dicarboxylic acid component composed of terephthalic acid and diol component composed of 20-35 mole% of 1,4-cyclohexanedimethanol and 65-80 mole% of ethylene glycol as a major component; 1-17 parts by weight of an acrylic rubber type modifying agent and 1-3 parts by weight of a lubricant.

[0006]

This invention also provides a polyester resin composition characterized by containing 100 parts by weight of a non-crystalline polyester resin comprising a dicarboxylic acid component composed of terephthalic acid and diol component composed of 20-35 mole% of 1,4-cyclohexanedimethanol and 65-80 mole% of ethylene glycol as a major component; 0.5-17 parts by weight of an acrylic rubber type modifying agent, 0.5-10 parts by weight of an acrylic processing aid material having methyl methacrylate as a main component and 1-3 parts by weight of a lubricant.

[0007]

[Preferred Embodiment of the Invention]

This invention is explained in detail as follows. The non-crystalline polyester used as a main component of the resin components of the polyester resin composition of this invention comprises a dicarboxylic acid component of consisting terephthalic acid and diol component

containing 20-35 mole% of 1,4-cyclohexanedimethanol and 65-80 mole% of ethylene glycol. Specifically, there are commercially available products such as trade name "PETG 6763" (copolyester of terephthalic acid as a dicarboxylic acid component and diol component comprising 30 mole% of 1,4-cyclohexanedimethanol and 70 mole% of ethylene glycol copolymerized) and trade name "Provista" (copolyester of terephthalic acid as a dicarboxylic acid component, diol component comprising 30 mole% of 1,4-cyclohexanedimethanol and 70 mole% of ethylene glycol and extremely small amount of the 3<sup>rd</sup> component copolymerized having high melt viscosity). In addition to the above non-crystalline polyester, it is also possible to use a crystalline, low-crystalline or another non-crystalline polyester resin. Specific examples include PET, PBT, PBTI, PETI resins, etc. If the total amount of those polyester resins is 100 parts by weight, the amount of the above non-crystalline polyester to be compounded is in the range of 60-100 parts by weight, preferably 80-100 parts by weight. If the amount of the above non-crystalline polyester to be compounded is below 80 parts by weight, the amount of the additive required to raise the melt viscosity is increased, and it is not desirable.

[0008]

The acrylic rubber-type modifying agent compounded in the above polyester resin composition comprises typically rubber particles of a multilayer structure consisting a core portion of acrylic rubber obtained by polymerization of acrylate such as butyl acrylate with a small amount of a cross-linking monomer and shell portion of a vinyl monomer such as methyl methacrylate, acrylonitrile, styrene, etc., graft-polymerized to the core portion. For example, there are conveniently usable commercially available products such as "HIA-80" manufactured by Kureha Chemical Co., "Acryloid KM-330" manufactured by Rohm & Haas Co., "Metablen W-300" and "Metablen W-530" manufactured by Mitsubishi Rayon Co., "Paraphase ME-120" manufactured by Kurare Co., etc. The amount of this acrylic rubber-type modifier to be used is in the range of 1-17 parts by weight (if an acrylic processing aid material is used, it is in the range of 0.5-17 parts by weight), preferably in the range of 1.5-15 parts by weight per 100 parts by weight of polyester. As a result of compounding with an amount within this range, the melt viscosity of the composition can be elevated, consequently, the composition in its gelated state by heating can be easily transferred, and the quantitative feeding accuracy to calendering rollers is improved im-

proving sheet thickness accuracy. If the amount is less than 1 part by weight, the above effects are not achievable, and on the other hand, if the amount is over 17 parts by weight, the surface properties of sheets prepared are rather liable to be damaged. Therefore, it is not desirable.

[0009]

As a lubricant compounded into the above polyester resin composition, there are hydrocarbon lubricants such as paraffin wax, olefin wax, etc.; higher fatty acid lubricants such as stearic acid, etc.; metal soap lubricants such as calcium stearate, etc.; and ester lubricants such as montanate wax, etc. They may be used alone or as a mixture of 2 or more kinds.

[0010]

If the amount of such a lubricant to be compounded is too small, there is no effect of compounding it, and the problem of the adhesiveness of polyester resins on calender rollers cannot be solved. On the other hand, if the amount is too large, it is liable to be seeped out on the sheet surface damaging the printability, and it is not desirable as an article of trade. Therefore, the amount of such a lubricant to be used in this invention is in the range of 0.5-3 parts by weight, preferably 1-2.5 parts by weight per 100 parts by weight of polyester.

[0011]

The acrylic processing aid material to be compounded in this invention is preferably a copolymer of acrylic acid, acrylate such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, etc., and methacrylate such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, etc., as a main component. Specifically, there are, for example, "Metablen P-551" and "Metablen P-530A" manufactured by Mitsubishi Rayon Co., "Kaneace PA-30" and "Kaneace PA-100" manufactured by Kanegafuchi Chemical Industry Co., etc.

[0012]

The amount of such an acrylic processing aid material to be compounded is in the range of 0.5-10 parts by weight, preferably 0.5-8 parts by weight and optimally 1-6 parts by weight per

100 parts by weight of polyester. If the amount compounded is too small, the desired effects providing a sliding property and increasing melt viscosity are not exhibited, and it becomes difficult to obtain a thin sheet having a uniformly smooth surface. On the other hand, if the amount compounded is too large, there is a risk of inviting a disturbed flow in the bank of calendering rollers, and it is liable to damage the surface properties. Therefore, it is not desirable.

[0013]

Furthermore, it is also possible to compound various additives used conventionally such as pigments, hindered amine light stabilizers, UV absorbents, antioxidants, antistatic agents, inorganic or organic fillers, compatible resins, etc.

[0014]

The polyester sheet of this invention can be prepared by compounding respective amounts of resin component containing the non-crystalline polyester described above as a main component, acrylic rubber-type modifier, lubricant, if necessary, acrylic processing aid material and various additives described above, and the mixture is kneaded to obtain a molding mixture, which is subsequently processed by carrying out calendering to obtain a sheet. The temperature of calendering rollers is generally in the range of 160-190°C, preferably 170-190°C.

[0015]

[Application Example]

This invention is explained specifically in detail by using application and comparative examples as follows, but this invention is not necessarily limited to these application examples. Incidentally, various evaluation items were evaluated under the following conditions and procedures.

[0016]

(1) Calendering processability



A calendering device with 4 calender rollers of 24 inch diameter was used to prepare sheets with a width of 1500 mm and thickness of 0.05 mm, 0.07 mm, 0.1 mm, 0.15 mm, 0.2 mm or 0.3 mm.

⊙: it is possible to prepare sheets of all thickness settings in the range of 0.05-0.3 mm.

O: it is possible to prepare sheets of thickness settings in the range of 0.07-0.3 mm.

Δ: it is possible to prepare sheets of thickness settings in the range of 0.2-0.3 mm.

X: it is possible to prepare only a sheet of 0.3 mm thick.

XX: it is impossible to prepare a sheet of any of those thickness settings.

[0017]

## (2) Thickness accuracy

The thinnest sheets among those prepared in (1) calendering processability were used, the thickness measurement was carried out at 10 points in the width direction and repeated 10 times for every 10 m in the length direction, and the fluctuation was determined.

O: within  $\pm 3\%$

Δ: within  $\pm 7\%$

X: within  $\pm 10\%$

[0018]

## (3) High-temperature embossing

A treatment with an embossing roller having a concavo-convex depth of 20  $\mu\text{m}$  and surface temperature in the range of 110-150°C was carried out, and the maximum embossing roller surface temperature enabling 80% or more of the depth on the sheet surface was measured.

O: 140°C or above

Δ: 115°C or above but below 140°C

X: below 115°C

[0019]

Application Example 1

To 100 parts by weight of a non-crystalline polyester resin ("Provista" manufactured by Eastman Chemical Co.), 2 parts by weight of an acrylic rubber modifier ("HA-80" manufactured by Kureha Chemical Industry Co.), 1.5 parts by weight of a lubricant (montanate wax "G431L" manufactured by Clariant (Japan) Co.), and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was used for the mixture obtained to prepare polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm having excellent transparency at 175°C. The calendering processability, thickness accuracy and high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0020]

Application Example 2

To 100 parts by weight of a non-crystalline polyester resin ("PETG 6763" manufactured by Eastman Chemical Co.), 5 parts by weight of an acrylic rubber modifier ("HA-80" manufactured by Kureha Chemical Industry Co.), 1.5 parts by weight of a lubricant (acrylate oligomer LS-12 manufactured by Asahi Chemical Co.) and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was used for the mixture obtained to prepare polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm having excellent transparency at 175°C. The calendering processability, thickness accuracy and high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0021]

Application Example 3

To 100 parts by weight of a non-crystalline polyester resin ("PETG 6763" manufactured by Eastman Chemical Co.), 5 parts by weight of an acrylic rubber modifier ("HA-80" manufactured by Kureha Chemical Industry Co.), 2 parts by weight of acrylic processing aid material ("Kaneace PA-100" manufactured by Kanegafuchi Chemical Industry Co.), 1.5 parts by weight of a lubricant (acrylate oligomer LS-12 manufactured by Asahi chemical Co.) and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was used for the

mixture obtained to prepare white polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm having excellent transparency at 180°C. The calendering processability, thickness accuracy and high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0022]

#### Application Example 4

To 100 parts by weight of a non-crystalline polyester resin ("PETG 6763" manufactured by Eastman Chemical Co.), 12 parts by weight of an acrylic rubber modifier ("HA-80" manufactured by Kureha Chemical Industry Co.), 2 parts by weight of acrylic processing aid material ("Metablen P-530A" manufactured by Mitsubishi Rayon Co.), 1.5 parts by weight of a lubricant (acrylate oligomer LS-12 manufactured by Asahi chemical Co.) and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was used for the mixture obtained to prepare white polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm having excellent transparency at 180°C. The calendering processability, thickness accuracy and high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0023]

#### Application Example 5

To 100 parts by weight of a polyester component comprising 80 parts by weight of a non-crystalline polyester resin ("Provista" manufactured by Eastman Chemical Co.) and 20 parts by weight of PETI resin (Toyobo Vylon Co. "GM500", copolyester comprising diethylene glycol and dicarboxylic acid component containing 30 mole% of isophthalic acid and 70 mole% of terephthalic acid), 7 parts by weight of an acrylic rubber modifier ("Metablen W-300" manufactured by Mitsubishi Rayon Co.), 3 parts by weight of acrylic processing aid material ("Kaneace PA-100" manufactured by Kanegafuchi Chemical Industry Co.), 1.5 parts by weight of a lubricant (montanate wax "G431L" manufactured by Clariant (Japan) Co.) and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was used for the mixture obtained to prepare white polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm having excellent transparency at 180°C. The calendering processability, thickness accuracy and

high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0024]

#### Application Example 6

To 100 parts by weight of a non-crystalline polyester resin ("Provista" manufactured by Eastman Chemical Co.), 5 parts by weight of an acrylic rubber modifier ("HA-80" manufactured by Kureha Chemical Industry Co.), 2 parts by weight of an acrylic processing aid material ("Kaneace PA-100" manufactured by Kanegafuchi Chemical Industry Co.), 1.5 parts by weight of a lubricant (acrylate oligomer LS-12 manufactured by Asahi chemical Co.) and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was used for the mixture obtained to prepare white polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm having excellent transparency at 180°C. The calendering processability, thickness accuracy and high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0025]

#### Application Example 7

To 100 parts by weight of a polyester component comprising 85 parts by weight of a non-crystalline polyester resin ("Provista" manufactured by Eastman Chemical Co.) and 15 parts by weight of PET ("EFG70" manufactured by Kanebo Gosen Co.), 5 parts by weight of an acrylic rubber modifier ("Metablen W-300" manufactured by Mitsubishi Rayon Co.), 4 parts by weight of acrylic processing aid material ("Metablen P-530A" manufactured by Mitsubishi Rayon Co.), 1.5 parts by weight of a lubricant (montanate wax "G431L" manufactured by Clalriant (Japan) Co.), 5 parts by weight of titanium oxide (inorganic filler) and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was used for the mixture obtained to prepare white polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm having excellent transparency at 180°C. The calendering processability, thickness accuracy and high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0026]

#### Comparative Example 1

To 100 parts by weight of a non-crystalline polyester resin ("PETG 6763" manufactured by Eastman Chemical Co.), 1.5 parts by weight of a lubricant (montanate wax "G431L" manufactured by Clariant (Japan) Co.) and 1 part by weight of phenolic antioxidant were added, a conventional calendering method was attempted for the mixture obtained to prepare transparent polyester resin sheets of a thickness in the range of 0.05 mm-0.3 mm at 160°C. The calendering processability, thickness accuracy and high-temperature embossing suitability were measured. The results obtained are shown in Table 1.

[0030]

#### Comparative Example 2

The same procedures and conditions as those in the comparative example 1 were used except that the calendering temperature was set at 175°C to attempt to prepare transparent polyester resin sheets having a thickness in the range of 0.05 mm-0.3 mm. The results obtained are shown in Table 1.

[0028]

[Table 1]

	Application Example							CE	
	1	2	3	4	5	6	7	1	2
Polyester resin • Provista • PETG 6763 • PET • PBTI	100	100	100	100	80 20	100	85 15	100	100
Acrylic rubber-type modifier • Metablen W-300 • HIA-80	2	5	5	12	7	5	5		
Acrylic processing aid material • Metablen P-530A • Kaneace PA-100			2	2	3	2	4		
Lubricant • G431L • LS-12	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Evaluation									
(1) Calendering processability	○	◎	◎	◎	◎	◎	◎	△	XX
(2) Thickness accuracy	○	○	○	○	○	○	○	△	—
(3) High-temperature embossing	○	○	○	○	○	○	○	△	—

CE: comparative example

[0029]

## [Effects of the Invention]

According to this invention, it has become possible to produce previously impossible thin polyester resin sheets of 0.05-0.2 mm thick having excellent transparency by carrying out calendering. Moreover, it is also possible to prepare colored polyester resin sheets by compounding fillers or coloring agents. Compared with the previous sheet preparation by carrying out extrusion, the sheet production speed is drastically improved, and the sheet thickness accuracy is also effectively improved.